

(19)



Eur pâisches Pat namt

Eur pean Pat nt Offic

Offi e uropé n des br v ts



(11)

EP 0 703 253 A1

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:  
27.03.1996 Bulletin 1996/13

(51) Int Cl. 6: C08F 297/08, C08L 53/00

(21) Application number: 95306721.2

(22) Date of filing: 22.09.1995

(84) Designated Contracting States:  
DE FR GB IT

(72) Inventor: Terano, Minoru  
Nomi-gun, Ishikawa-ken (JP)

(30) Priority: 22.09.1994 JP 228040/94

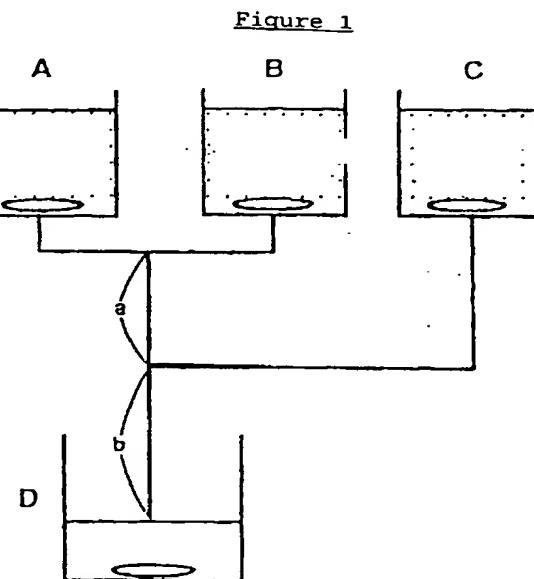
(74) Representative: Woods, Geoffrey Corlett et al  
J.A. KEMP & CO.  
14 South Square  
Gray's Inn  
London WC1R 5LX (GB)

### (54) Olefinic block copolymer and production process thereof

(57) An olefin block copolymer in which an ethylene or propylene polymer is chemically bonded with a copolymer of ethylene and propylene may be prepared by a process which comprises

(a) polymerising a first olefin, which is ethylene or propylene, in the presence of a catalyst to give a reaction product comprising a polymer of the first olefin and unreacted first olefin; and

(b) polymerising a second olefin, which is ethylene or propylene and which is different from the first olefin, in the presence of a catalyst and the reaction product of step (a), such that a copolymer of the first and second olefins is produced and chemical bonds are formed between the said copolymer and the said polymer of the first olefin.



## Description

The present invention relates to a polypropylene-b-poly(ethylene-co-propylene) or a polyethylene-b-poly(ethylene-co-propylene), and a production process thereof. More specifically, the invention relates to a polypropylene-b-poly(ethylene-co-propylene) or a polyethylene-b-poly(ethylene-co-propylene), that has a superior impact strength and is useful as a compatibilizer for a crystalline polyolefin and an amorphous polyolefin, and a production process of the block copolymer. Furthermore, the present invention relates to a polyolefin material, wherein a polymer in which a polypropylene or a polyethylene and poly(ethylene-co-propylene) are repeated and polypropylene-b-poly(ethylene-co-propylene) or a polyethylene-b-poly(ethylene-co-propylene) are blended in either a polyethylene or a poly(ethylene-co-propylene) or in their mixture.

Polyolefins such as polypropylenes and polyethylenes are massively produced and consumed since they are inexpensive and excellent in processability and various physical properties such as mechanical strength, heat resistance, chemical resistance and electrical insulation. However, for example, polypropylene is poor in impact strength while it is relatively excellent in stiffness; this disadvantage is improved by blending an amorphous poly(ethylene-co-propylene) that is excellent in impact strength. In the conventional block type copolymers, the matrix comprising polypropylene and the domain comprising poly(ethylene-co-propylene) are separated, which causes lowering the physical properties. These problems have been desired to be improved. It is expected that a block copolymer in which a polypropylene and a poly(ethylene-co-propylene) are chemically bonded might overcome these problems and provide a material having more excellent characteristics.

Conventionally, so-called block type copolymers have been known as one type of a polypropylenes that are composed of a polypropylene and poly(ethylene-co-propylene). The conventional block type copolymer is produced by a two-step process comprising, for example, the synthesis of a polypropylene for 30 minutes to several hours in a first polymerization vessel, followed by the synthesis of a poly(ethylene-co-propylene) for also 30 minutes to several hours in a second polymerization vessel. Considering the period of time for forming one polymer chain, chemical bonds between the polypropylene and the poly(ethylene-co-propylene) are not formed in so-called block type copolymers. They exist in a micro-blend state; a true block copolymer as defined in polymer chemistry is not formed, thus satisfactory characteristics as targeted are not always realized.

In view of this problem, the present inventors have studied, in various respects, how to get a novel true block copolymer that is a true block copolymer having a polypropylene or a polyethylene chemically bonded with a poly(ethylene-co-propylene) and that has not been conventionally available. As a result, the present inventors have noted that a polymerization reaction of an olefin using a transition metal catalyst normally completes within one second for one polymer chain, and have found that a true block copolymer can be obtained by a polymerization in a short period using a special method. An object of the present invention is to provide true block copolymers and a polyolefine materials in which the true block copolymer exists in blend with polyolefins, and to provide a process for producing them.

Essence of the present invention lies in an olefin block copolymer wherein a polypropylene or a polyethylene and a poly(ethylene-co-propylene) are chemically bonded; a polyolefin material characterized by that an olefin block copolymer wherein a polypropylene or a polyethylene and a poly(ethylene-co-propylene) are chemically bonded is present in blend with any one of a polypropylene, a polyethylene and a poly(ethylene-co-propylene) or in blend with their mixture; and providing a process for producing them.

Accordingly, the present invention provides an olefin block copolymer which comprises a polymer of a first olefin which is ethylene or propylene, and a copolymer of ethylene and propylene, wherein the said polymer is chemically bonded to the said copolymer.

The invention further provides a process for producing an olefin block copolymer, which process comprises (a) polymerising a first olefin, which is ethylene or propylene, in the presence of a catalyst to give a reaction product comprising a polymer of the first olefin and unreacted first olefin; and (b) polymerising a second olefin, which is ethylene or propylene and which is different from the first olefin, in the presence of a catalyst and the reaction product of step (a), such that a copolymer of the first and second olefins is produced and chemical bonds are formed between the said copolymer and the said polymer of the first olefin.

Typically the catalyst used in step (a) and/or step (b) is a Ziegler catalyst, for instance comprising a titanium trihalide procatalyst and an aluminium alkyl cocatalyst. A metallocene catalyst, for instance a metallocene of Zr or Hf is also preferred.

When the first olefin is polyethylene, the second olefin is polypropylene. The block copolymer then comprises an ethylene polymer chemically bonded to a copolymer of ethylene and propylene. When the first olefin is polypropylene, the second olefin is polyethylene. The block copolymer then comprises a propylene polymer chemically bonded to a copolymer of ethylene and propylene.

The present invention will be further described with reference to the accompanying drawings, wherein:

Fig. 1 is a schematic representation of a polymerization process in which vessel A contains toluene, catalyst and propylene; vessel B contains toluene, co-catalyst and propylene; vessel C contains toluene and ethylene; vessel D

contains ethanol; and a and b denote polymerisation regions.

Fig. 2 is a schematic representation of a polymerization process in which vessel A contains toluene, a metallocene catalyst, an alkylating agent and a cationic agent; vessel B contains toluene and propylene; vessel C contains toluene and ethylene; vessel D contains ethanol; and a and b denote polymerisation regions.

Fig. 3 is a schematic representation of a process in which vessel A contains toluene, catalyst and propylene; vessel B contains toluene, co-catalyst and propylene; vessel C contains toluene and ethylene; arrow E indicates entry of propylene, ethylene and/or a gas mixture of propylene and ethylene; arrow F indicates exit of exhaust gas; and a and b denote polymerisation regions; and

Fig. 4 is a Gas Phase Chromatography (GPC) curve for the polypropylene-b-poly(ethylene-co-propylene) obtained in Example 1, in which the x axis represents the elution time.

Now the present invention is explained in detail. According to the present invention, a polyethylene-b-poly(ethylene-co-propylene) or a poly-propylene-b-poly(ethylene-co-propylene) is excellent in impact strength, and exhibits, in addition, useful characteristics as compatibilizer for a crystalline polyolefin and an amorphous polyolefin. In the case of a polypropylene, high isotacticity is preferred, however, it is not limited to such one. When the block copolymer according to the present invention is synthesized, polypropylene, a polyethylene or a poly(ethylene-co-propylene) can be coexistent by controlling the polymerization process and condition.

In a process for producing such polymers, using a catalyst such as titanium tetrachloride supported on magnesium chloride in combination with a cocatalyst such as triethylaluminum, or a metallocene compound of hafnium or zirconium in combination with methylaluminoxane or a boron compound, a polypropylene or polyethylene is synthesized at first within a small tube for 0.01 to 10 seconds and subsequently a poly(ethylene-co-propylene) is synthesized continuously in nearly same period of time. In the process, the length of the block chains may be varied by altering respective periods. Repeat of these steps twice or more is also possible; furthermore, the polymerization periods in the repeat step may be made longer period (1 minute to 2 hours approximately).

As for the catalyst, various catalysts can be used, other than the titanium tetrachloride supported on magnesium chloride mentioned above, including titanium trichloride catalysts, metallocene catalysts and other types. In addition, these catalysts may be preliminarily treated with a cocatalyst such as alkylaluminums, activating agents such as methylaluminoxane, and agents for making cationic such as a boron compound; so-called electron donor compounds such as an aromatic ester and silicon compounds may be coexistent.

As for the cocatalyst used in the present invention, various alkylaluminums, alkylaluminum halides, and alkylaluminum hydrides may be used. Examples of the alkylaluminum include trialkylaluminum such as triethylaluminum and triisobutylaluminum; examples of the alkylaluminum halide include diethylaluminum chloride and ethylaluminum sesquichloride; and examples of the alkylaluminum hydride include diethylaluminum hydride and diisobutylaluminum hydride.

The polymerization temperature is not limited in particular, however, normally in a range of 0°C through 200°C.

The solvent used is not limited in particular, however, normally toluene, xylene, hexane or heptane is used.

Now, examples of the polymerization process according to the present invention will be described in more detail with reference to drawings.

Fig. 1 illustrates a polymerization process of an olefinic copolymer in which the polypropylene and poly(ethylene-co-propylene) are chemically bonded.

In Fig. 1, a toluene slurry of a catalyst is contained in vessel A, and a toluene solution of triethylaluminum is contained in vessel B; propylene is dissolved in both vessels. In vessel C, ethylene-saturated toluene is contained. Liquids in respective vessels flow out from Teflon tubes fitted to the down parts. At a first step, the effluents from vessels A and B are joined to synthesize a polypropylene. Symbol "a" indicates the polymerization region. The flow out of polymerization region "a" contains unreacted propylene and the catalyst in addition to the polypropylene; therewith the toluene solution of ethylene from vessel C joins, and a poly(ethylene-co-propylene) is produced in polymerization region "b" at end of the polypropylene.

Subsequently, the flow is introduced into vessel C that contains ethanol, and the catalyst is deactivated. Thereby, a polypropylene-b-poly(ethylene-co-propylene) results. Composition of the product polymer can be controlled by adjusting the length of polymerization regions "a" and "b" and the amount of propylene in vessels A and B and of ethylene in vessel C.

Fig. 2 is almost the same as Fig. 1 ; a metallocene catalyst, an alkylating agent, and an agent for making cation are solved in vessel A, propylene-saturated toluene is contained in vessel B. and ethylene-saturated toluene is contained in vessel C. Liquids in respective vessels flow out from Teflon tubes fitted to the down parts. The reactions in polymerization region "a" and "b" are same as in Fig. 1; a desired block copolymer was obtained in the same way as in Fig. 1.

In Fig. 3 similarly to Fig. 1, a toluene slurry of a catalyst is contained in vessel A, and a toluene solution of an cocatalyst is contained in vessel B; propylene is dissolved in both vessels. In vessel C, toluene in which ethylene is dissolved is contained. After getting a polypropylene-b-poly(ethylene-co-propylene) similarly to the case of Fig. 1, propylene, ethylene, or a mixed gas of propylene and ethylene are, individually or successively if required, introduced into

## EP 0 703 253 A1

vessel D to polymerize. Thereby, these monomers polymerize to produce a polyolefin material. Thus, the polyolefin material was obtained in which the polypropylene-b-poly(ethylene-co-propylene) polymerized preliminarily was mixed with a polypropylene and/or a polyethylene and/or a poly(ethylene-co-propylene).

5 Examples 1 to 3 and Comparative Example

A polypropylene-b-poly(ethylene-co-propylene) was prepared using the apparatus of Fig. 1.

One hundred millilitres of a toluene slurry containing 1.3 g of a catalyst was accommodated in vessel A, in which propylene was dissolved to a concentration of 0.68 mol/l. The catalyst used was prepared as follows.

10 Magnesium chloride and ethyl benzoate were coground in a vibrating mill for 30 hours, then treated with titanium tetrachloride at 90°C for 2 hours; thereafter, the product was washed with heptane which was finally replaced with toluene.

In vessel B, 100 ml of a toluene solution of 70 mmol/l triethylaluminum was charged and propylene was dissolved to a concentration of 0.68 mol/l. In vessel C, 100 ml of a toluene solution with a 0.2 mol/l ethylene content was accommodated.

15 Table 1 shows the time of polymerization in reaction regions "a" and "b", as depicted in Figure 1, and the number average molecular weight and molecular weight distribution of the resultant polymers. The number average molecular weight and molecular weight distribution were determined by Gas Phase Chromatography (GPC). The values were estimated to polystyrene standards.

20

Table 1

Synthesis of polypropylene-b-poly(ethylene-co-propylene).					
Example	Polymerization Time (seconds)		$M_n \times 10^3$	$M_w / M_n$	Ethylene content mol %
	region "a"	region "b"			
1	0.065	0.065	11	3.8	
2	0.060	0.120	15	3.6	25
3	0.130	0.130	20	3.3	

30

The GPC curve for the resultant polypropylene-b-poly(ethylene-co-propylene) is given in Figure 4.

Next, the polypropylene-b-poly(ethylene-co-propylene) prepared in Example 2 and separately prepared 0.19 g of a polypropylene (polymerization period: 0.08 seconds) blended with 0.38 g of a poly(ethylene-co-propylene) (polymerization period: 0.13 seconds) (this blend is referred to as Comparative Example) were respectively charged into flasks, to each of which 50 ml of n-heptane was added. Stirring was applied under nitrogen atmosphere at room temperature (about 25°C) for 24 hours. Thereafter, each was subjected to centrifugal separation (3000 rpm, for 8 minutes), and supernatant was removed. This sequence of operations was repeated three times, then the extraction residues were dried at 60°C under vacuum for 2 hours; yields of the resultant polymers were measured. Table 2 shows the results.

40

Table 2

Results of n-heptane extraction experiments		
Sample	Weight before extraction (g)	Weight after extraction (g)
Example 2	0.57	0.52
Comparative Example	0.57	0.19

45

The sample from Example 2 retained most polymer, whereas the Comparative Example sample retained only polypropylene and the poly(ethylene-co-propylene) was extracted.

## 50 Example 4

A polypropylene-b-poly(ethylene-co-propylene) was prepared by using the apparatus of Fig. 2.

In vessel A, 100 ml of toluene solution was charged which contained a polymerization catalyst consisting of 0.26 g of dimethylsilylene bis(2,3,5-trimethylcyclopentadienyl)zirconium dichloride, 18 mmol of triisobutyl aluminum, and 0.66 mmol of N,N-dimethylanilinium tetra(pentafluorophenyl)borate, and the content was maintained for 2 minutes at 30°C with agitation. Propylene in vessel B and ethylene in vessel C were respectively dissolved in 100 ml of toluene under a pressure of 8 kgf/cm<sup>2</sup>G. Thereafter, propylene in "a", and ethylene and propylene in "b" were respectively polymerized

55

at 30°C for 0.5 seconds; 1.33 g of a polymer was obtained thereby.

#### Example 5

5 A Polyolefin material containing a polypropylene-b-poly(ethylene-co-propylene) was prepared by using the apparatus of Fig. 3.

One hundred milliliters of a toluene slurry containing 1 g of the same catalyst as used in Example 1 was charged, and propylene was solved to be 0.68 mol/l.

10 In vessel B, a toluene solution containing 14 mmol of triethylaluminum and 0.7 mmol of cyclohexyl methyl dimethoxysilane was pressured by propylene to be 0.68 mol/l also. In vessel C, ethylene was dissolved into 100 ml of toluene to be 0.21 mol/l. As the first step, propylene was polymerized in polymerization region "a" at a temperature of 30°C for 0.1 seconds, and the synthesis of poly(ethylene-co-propylene) bonded with the propylene was made in "b" for 0.1 seconds. Then in vessel D, polypropylene was synthesized at 80°C for 10 minutes followed by poly(ethylene-co-propylene) for 15 minutes. Thereby, 42.6 g of an polyolefin material that contained 0.37 g of polypropylene-b-poly(ethylene-co-propylene) was obtained.

15 As explained hereinabove, the synthesis of a polyolefin block copolymer that has been impossible by conventional polymerization processes and technologies was successful according to the present invention. The characteristic of the novel block copolymer was different from the conventional block type copolymers due to the chemical bond of a polypropylene or a polyethylene with a poly(ethylene-co-propylene). The polymer is very useful as a new plastic and a compatibilizer for a crystalline polyolefin and an amorphous polyolefin.

#### Claims

25 1. An olefin block copolymer which comprises a polymer of a first olefin which is ethylene or propylene, and a copolymer of ethylene and propylene, wherein the said polymer is chemically bonded to the said copolymer.

2. A block copolymer according to claim 1 which comprises a polypropylene chemically bonded to a poly(ethylene-co-propylene).

30 3. A block copolymer according to claim 1 which comprises a polyethylene chemically bonded to a poly(ethylene-co-propylene).

4. An olefin material which comprises an olefin block copolymer as defined in any one of claims 1 to 3 blended with a polymer of ethylene or propylene, a copolymer of ethylene and propylene, or a mixture thereof.

35 5. A process for producing an olefin block copolymer, which process comprises

40 (a) polymerising a first olefin, which is ethylene or propylene, in the presence of a catalyst to give a reaction product comprising a polymer of the first olefin and unreacted first olefin; and

45 (b) polymerising a second olefin, which is ethylene or propylene and which is different from the first olefin, in the presence of a catalyst and the reaction product of step (a), such that a copolymer of the first and second olefins is produced and chemical bonds are formed between the said copolymer and the said polymer of the first olefin.

6. A process according to claim 5 wherein a Ziegler catalyst is used as the polymerisation catalyst in step (a) or step (b).

7. A process according to claim 5 wherein a metallocene catalyst is used as the polymerisation catalyst in step (a) or step (b).

8. A process according to any one of claims 5 to 7 wherein step (a) or step (b) is repeated.

9. A process according to any one of claims 5 to 8 which further comprises  
55 (c) producing a polymer of ethylene or propylene, or a copolymer of ethylene and propylene, and blending the said polymer or copolymer with the block copolymer obtained in step (b).

10. An olefin block copolymer which comprises a polymer of a first olefin which is ethylene or propylene, and a copolymer

**EP 0 703 253 A1**

of ethylene and propylene, wherein the said polymer is chemically bonded to the said copolymer, the block copolymer being obtainable by a process as defined in any one of claims 5 to 8.

5

10

15

20

25

30

35

40

45

50

55

Figure 1

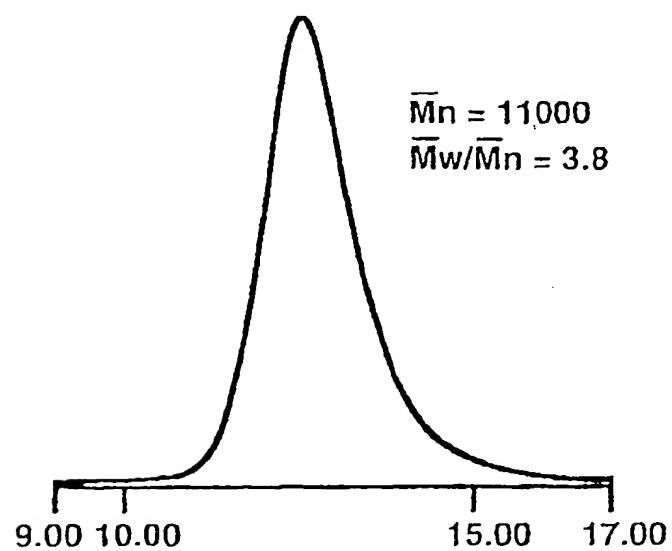
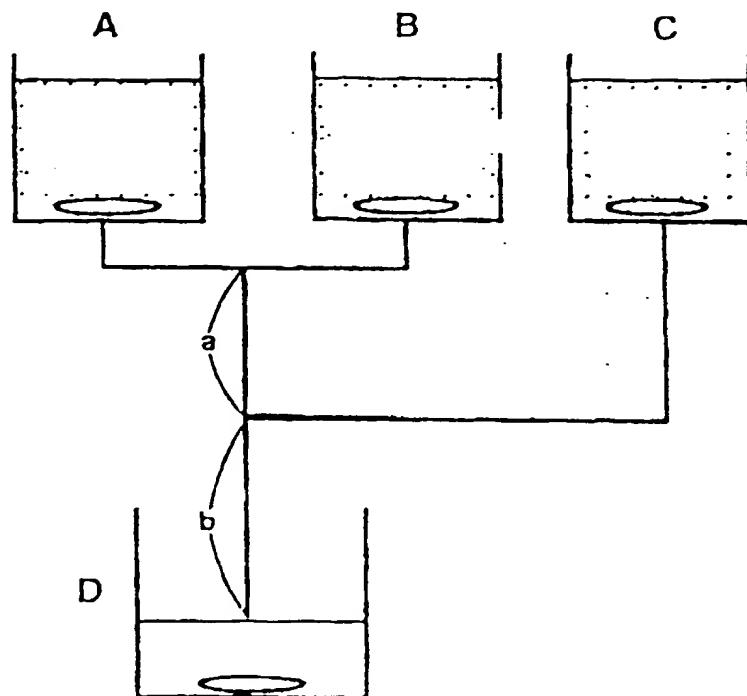


Figure 4

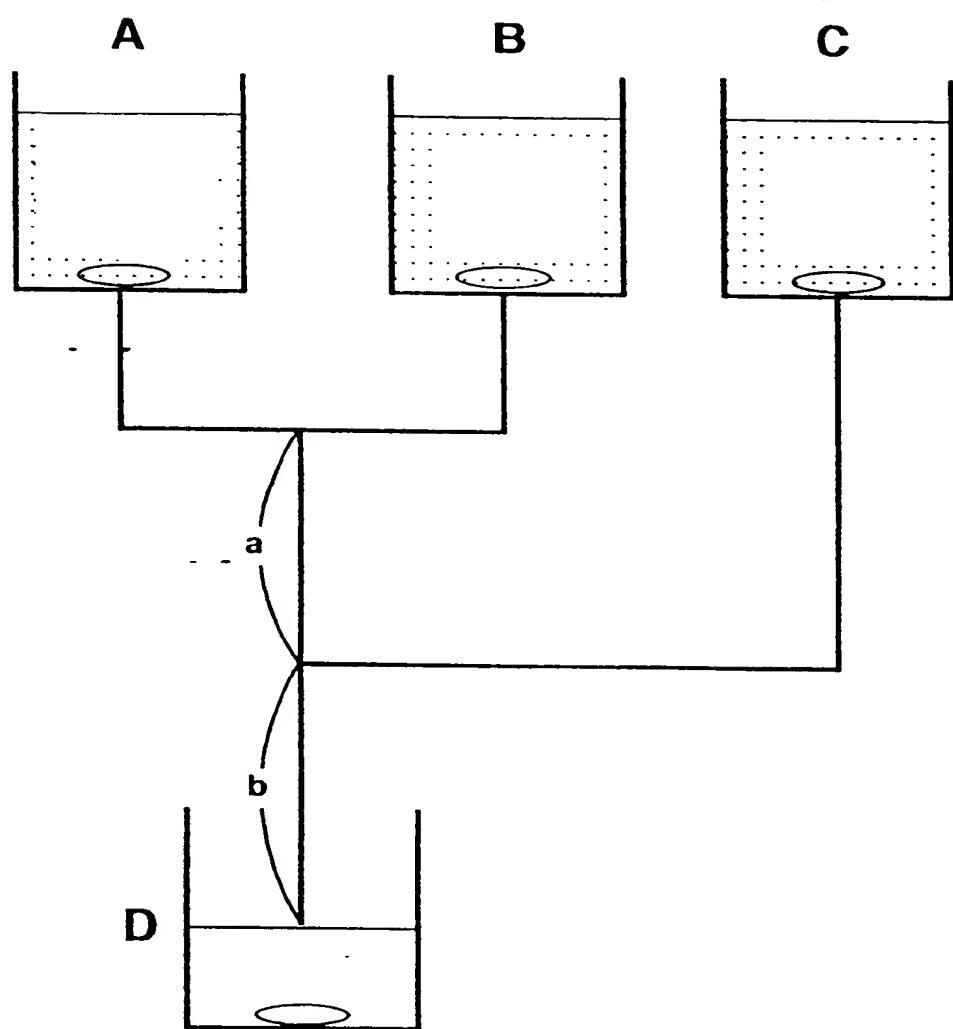


Figure 2

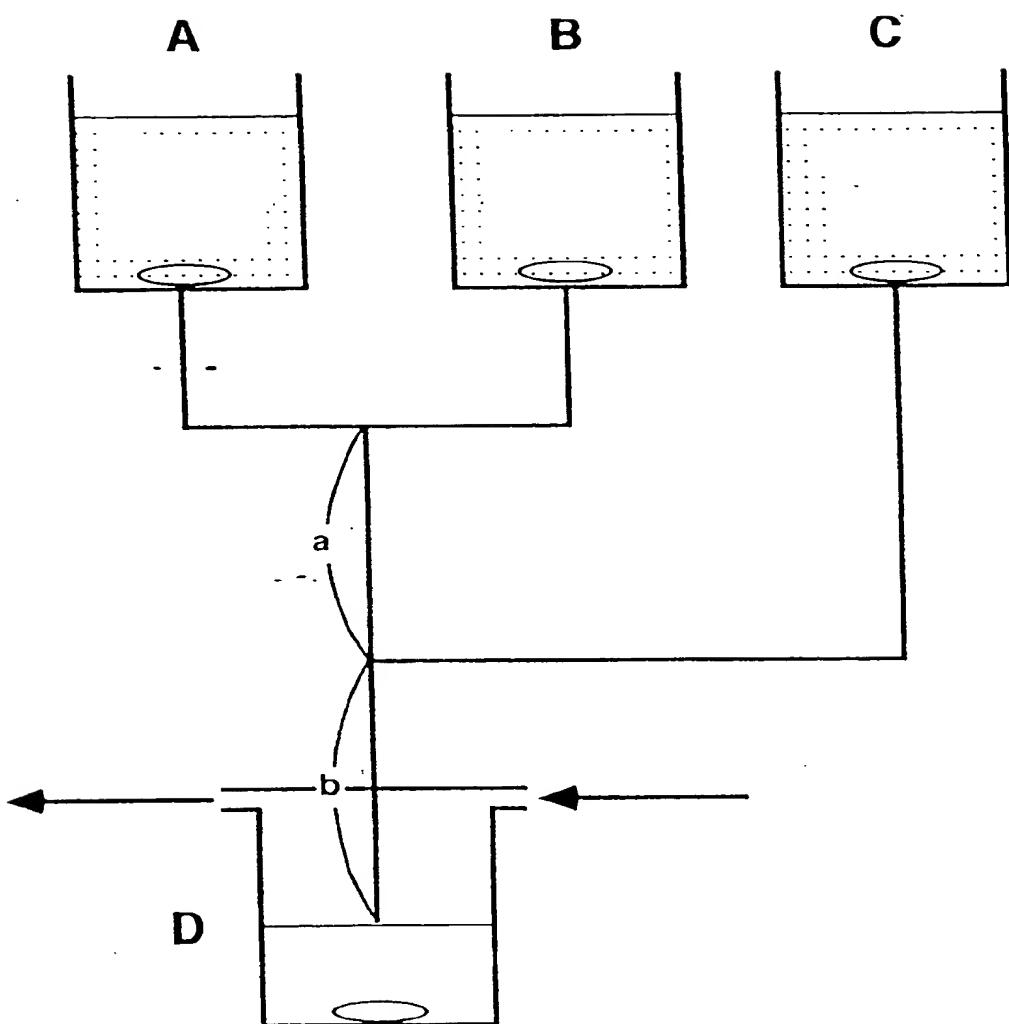


Figure 3



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 95 30 6721

DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)						
X	GB-A-2 184 128 (MITSUI TOATSU CHEM. INC.) * the whole document * ---	1,2,5,6, 10	C08F297/08 C08L53/00						
X	GB-A-2 055 388 (EL PASO POLYOLEFINS CO.) * the whole document * ---	1,2,5,6, 10							
X	EP-A-0 405 201 (MITSUI TOATSU CHEM. INC.) * the whole document * ---	1,2,4,5, 7,10							
X	EP-A-0 433 986 (HOECHST AG) * the whole document * ---	1,2,5,7, 10							
X	EP-A-0 433 990 (HOECHST AG) * the whole document * ---	1,2,5,7, 10							
X	DE-A-41 30 429 (BASF AG) * the whole document * -----	1,2,5,7, 10	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C08F						
<p>The present search report has been drawn up for all claims.</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>11 December 1995</td> <td>Glikman, J-F</td> </tr> </table> <p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone      Y : particularly relevant if combined with another document of the same category      A : technological background      O : non-written disclosure      P : intermediate document</p> <p>T : theory or principle underlying the invention      E : earlier patent document, but published on, or after the filing date      D : document cited in the application      L : document cited for other reasons      &amp; : member of the same patent family, corresponding document</p>				Place of search	Date of completion of the search	Examiner	THE HAGUE	11 December 1995	Glikman, J-F
Place of search	Date of completion of the search	Examiner							
THE HAGUE	11 December 1995	Glikman, J-F							